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(71) Applicant: MOTOROLA, INC.
Schaumburg, IL 60196 (US)

(72) Inventors:

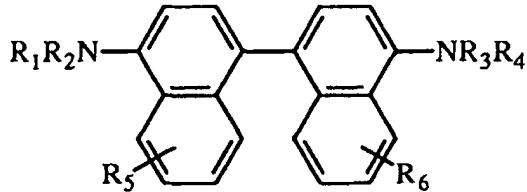
- Shi, Song Q.
Phoenix, Arizona 85044 (US)

- So, Franky
Tempe, Arizona 85284 (US)
- Lee, Hsing-Chung
Calabasas, California 91302 (US)

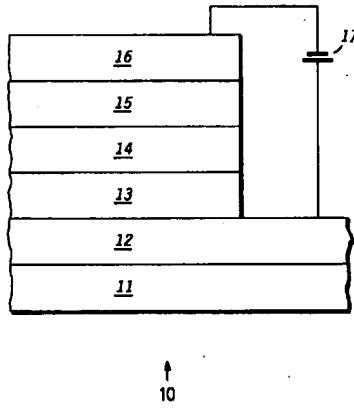
(74) Representative: Gibson, Sarah Jane et al
Motorola,
European Intellectual Property Operations,
Midpoint,
Alencon Link
Basingstoke, Hampshire RG21 7PL (GB)

(54) Organic electroluminescent device with new hole transporting materials

(57) An organic EL device including a cathode (16), an electron transporting layer (15), an emitting layer (14), a hole transporting layer (13) and an anode (12) laminated in sequence. The hole transporting layer (13) includes a substance represented by:



(Formula I)



where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.

Description**Field of the Invention**

5 This invention relates to an organic electroluminescence device and, more specifically, to a device with a new hole transporting material.

Background of the Invention

10 Organic electroluminescent (EL) devices are generally composed of three layers of organic molecules sandwiched between transparent and metallic electrodes, the three layers including an electron transporting layer, an emissive layer and a hole transporting layer. Organic EL devices are attractive owing to low driving voltage and a potential application to full color flat emissive displays. Though significant lifetime has been achieved in the prior art (See US Patent No. 4,720,432, entitled "Electroluminescent Device with Organic Luminescent Medium", issued January 19, 1988), further improvement is needed for applications where high brightness is required. In general, the hole transporting materials used in the hole transporting zone of an organic EL device are the most vulnerable parts which are susceptible to thermal degradation by physical aggregation or recrystallization.

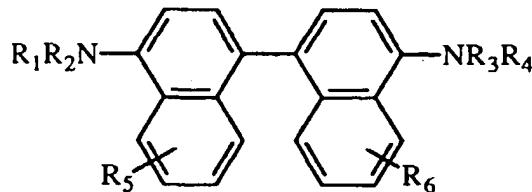
15 To address the thermal degradation problem of the hole transporting materials in an organic EL device, several schemes have been proposed: one being a double-layer hole transporting configuration (see US Patent 5,256,945, entitled "Organic Electroluminescent Element", issued October 26, 1993); one being usage of materials of high glass transition temperatures (US Patent 5,061,569, entitled "Electroluminescent Device with Organic Electroluminescent Medium", issued October 29, 1991).

20 It is a purpose of this invention to provide an organic EL device with a new hole transporting material, which has high thermal stability.

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Summary of the Invention

An organic EL device comprises a cathode, an electron transporting layer, an emitting layer, a hole transporting layer and an anode which are laminated in sequence, where said hole transporting layer is made of a substance represented by the following chemical formula I:



40 (Formula I)

45 where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.

Brief Description of the Drawing

50 The single figure is a simplified cross-sectional view of a light emitting diode in accordance with the present invention.

Description of the Preferred Embodiments

55 The present invention is directed to an organic light emitting device which, in general, consists of thin layers of organic molecules sandwiched between transparent and metallic electrodes.

The single Figure illustrates in a simplified cross-sectional view, one embodiment of an organic light emitting device (LED) 10. Organic LED 10 includes a transparent substrate 11 which in this specific embodiment is a glass or plastic plate having a relatively planar upper surface. A transparent electrically conductive layer 12 is deposited on the planar surface of substrate 11 so as to form a relatively uniform electrical contact. A hole transporting layer 13 made of organic

hole transporting material is deposited on the surface of conductive layer 12. An emissive organic layer 14 made of a host emissive material containing a guest fluorescent dopant is deposited onto the surface of layer 13. Then an electron transporting layer 15 made of an electron transporting material is deposited on the surface of layer 14 and a second electrically conductive layer 16 is deposited on the upper surface of layer 15 to form a second electrical contact.

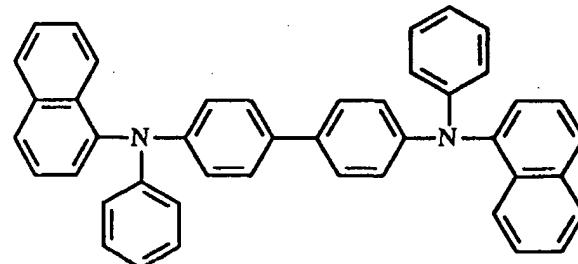
5 In this embodiment, conductive layer 16 is formed of any of a wide range of metals or alloys in which at least one metal has a work function less than 4.0 eV. By the proper selection of material for conductive layer 16, the work functions of the materials making up layers 15 and 16 are substantially matched to reduce the required operating voltage and improve the efficiency of organic LED 10. Additional information on work function matching is disclosed in a copending U.S. Patent Application entitled "Organic LED with Improved Efficiency", filed 12 September 1994, bearing
10 serial number 08/304,454, and assigned to the same assignee.

In this embodiment conductive layer 12 is a p-type contact and conductive layer 16 is an n-type contact. The negative terminal of a potential source 17 is connected to conductive layer 16 and the positive terminal is connected to conductive layer 12. When a potential is applied between layers 12 and 16 by means of potential source 17, electrons injected from the n-type contact (layer 16) are transported through organic layer 15 and into organic layer 14 (the emissive layer) and holes injected from the p-type contact (layer 12) are transported through organic layer 13 and into organic layer 14 (the emissive layer), where upon an electron and a hole recombination a photon is emitted.

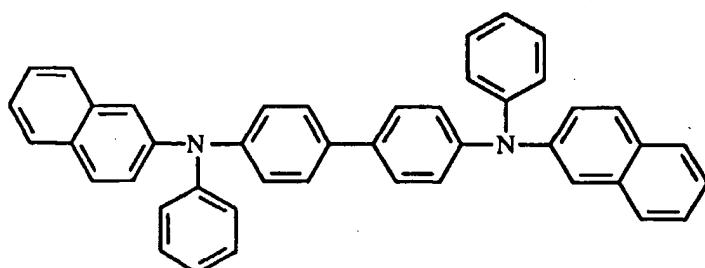
It has been recognized in the prior art that the hole transporting materials made up of tertiary aromatic amines are the least thermally stable materials in organic electroluminescent devices. Especially, when an organic EL device is driven at high electric current density, the hole transporting materials in the hole transporting layer tend to aggregate or reorganize to form islands, domains and pinholes. The change in film uniformity and homogeneity of hole transporting materials causes initially the gradual degradation in device luminance and eventually the device failure.

Generally, the glass transition temperature (T_g) of a material is an indicator for thermal stability of the resulting amorphous films. Higher glass transition temperature offers higher thermal stability for an amorphous film. A large molecule weight and strong steric hindrance to stacking are two of the main factors that determine the glass transition temperature of an organic material.

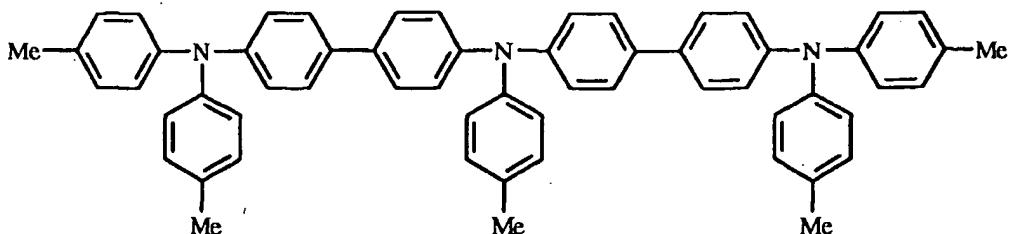
In an effort to improve the reliability of organic EL devices, Shirota (see *J. Phys. Chem.* 1993, **97**, 6240 and reference within) and Adachi (*Appl. Phys. Lett.*, 1995, **66** (20), 2679) have designed and prepared several symmetric globular tertiary aromatic amines with high T_g , yielding homogeneous amorphous films for organic EL devices applications. In the prior art, the following compounds represented by HMT-1, HMT-2, HMT-3 and HMT-4 are a few organic hole transporting materials with T_g above 75 °C and give excellent lifetimes when used in organic EL devices.



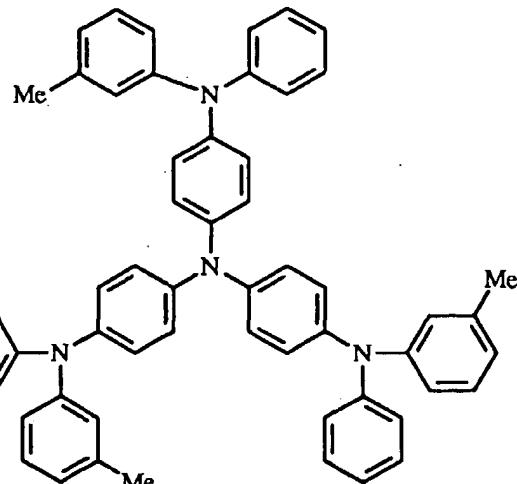
(HTM-1)



(HTM-2)



(HTM-3)

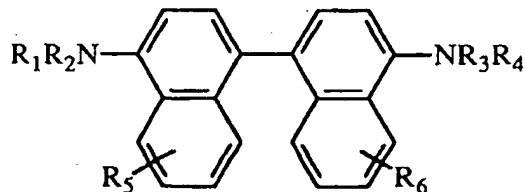


(HTM-4)

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It is a purpose of this invention to provide a new class of aromatic amines having high glass transition temperatures for use in organic light emitting diode.

According to present invention, an organic EL device as illustrated in LED 10 comprises a cathode, an electron transporting layer, an emitting layer, a hole transporting layer and an anode which are laminated in sequence, where 40 said hole transporting layer is made of a substance with central binaphthyl group represented by the following chemical formula:



(Formula I)

where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, 55 a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.

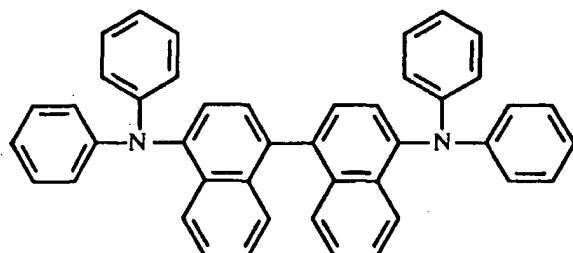
In this specific embodiment, it is desirable that the hole transporting material used in the hole transporting layer in organic EL device 10 has glass transition temperatures above 75 °C. However, it is preferred that hole transporting material having glass transition temperature greater than 90 °C is to be used to achieve a long lasting organic EL

device.

The following is a partial list of examples of aromatic tertiary amines satisfying the requirement of the present invention:

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(ATA-1)

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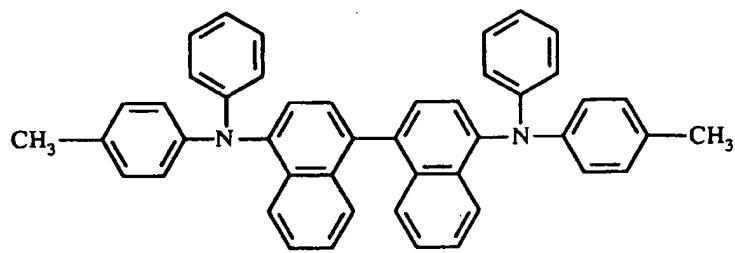
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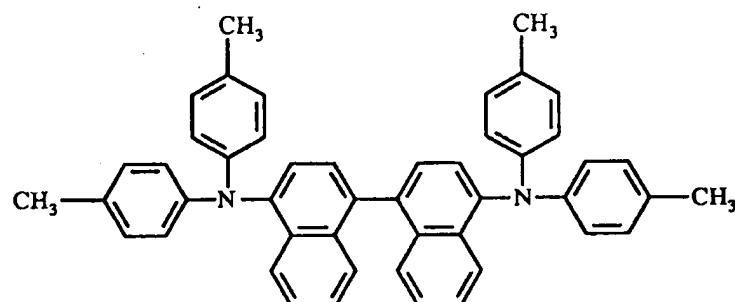
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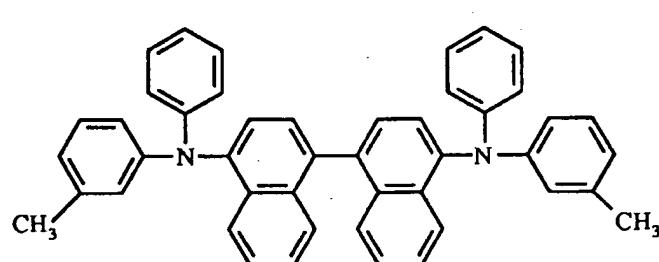
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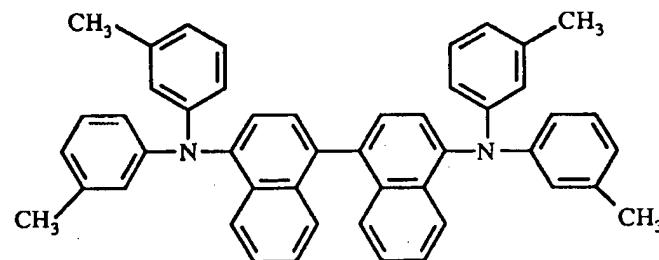
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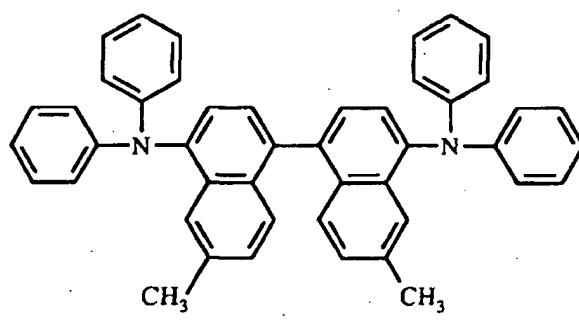
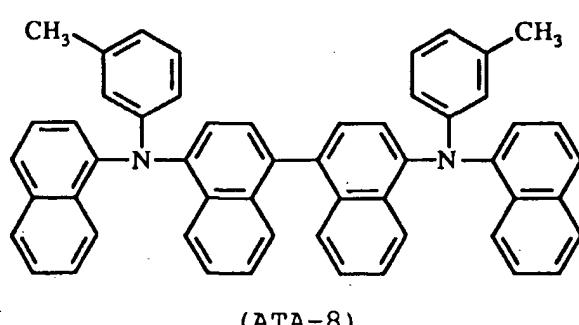
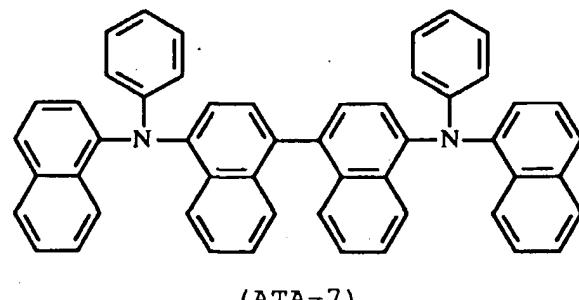
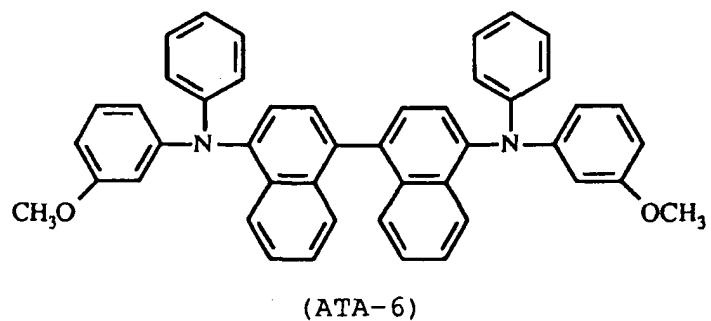
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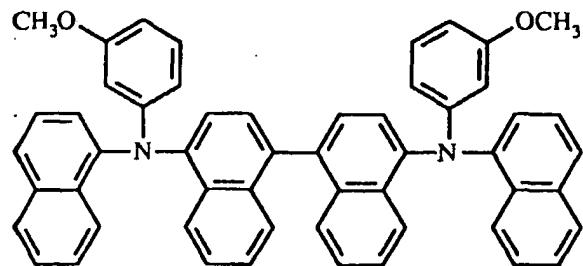


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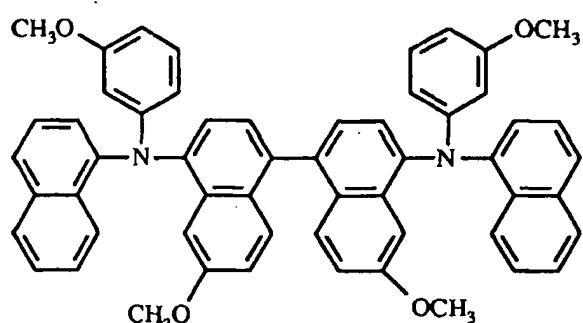


(ATA-5)





(ATA-10)



(ATA-11)

30 In one alternative embodiment, the hole transporting layer in LED 10 is composed of two layers of hole transporting materials, wherein, at least one layer of the hole transporting material is selected from the substance represent by formula I in accordance with the present invention.

35 In another alternative embodiment, the hole transporting layer in LED 10 is composed of a layer of mixed hole transporting materials, wherein, at least one of the hole transporting materials is selected from the substance represented by formula I in accordance with present invention.

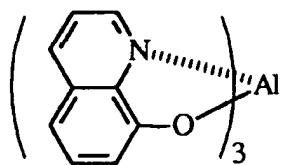
In this embodiment, the electron transporting layer 15 of LED 10 is preferred to, but not limited to, be selected from the following electron transporting materials:

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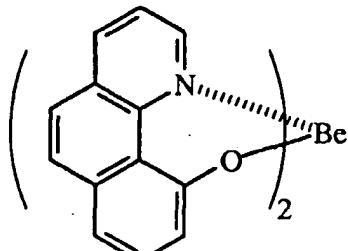
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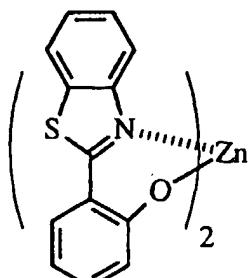
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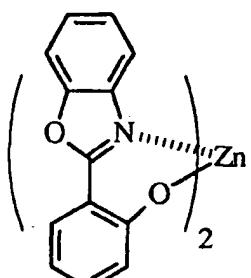
(Alq)



(BeBq)



(ZnSPB)



(ZnOPB)

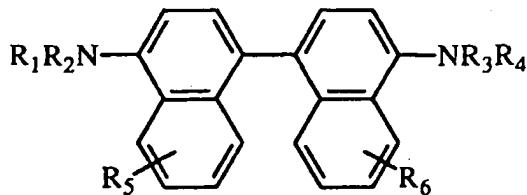
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The hole transporting materials used in the embodied organic EL device generally have high glass transition temperatures because of the rigid central binaphthyl group. Since higher glass transition temperature generally renders higher thermal stability for an amorphous film, the organic EL devices according to the present invention provide better reliability under high current density driving condition than normal organic EL devices.

55 While we have shown and described specific embodiments of the present invention, further modifications and improvements will occur to those skilled in the art. I desire it to be understood, therefore, that this invention is not limited to the particular forms shown and I intend in the appended claims to cover all modifications that do not depart from the spirit and scope of this invention.

Claims

1. An organic EL device comprising a cathode (16), an electron transporting layer (15), an emitting layer (14), a hole transporting layer (13) and an anode (12) laminated in sequence, wherein said hole transporting layer (13) includes
 5 a material represented by the following chemical formula I:



(Formula I)

where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.

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2. An organic electroluminescence device as claimed in claim 1, wherein the hole transporting material (13) has a glass transition temperature above 75 °C.

25 3. An organic electroluminescence device as claimed in claim 1, wherein the hole transporting material (13) is selected from the following materials:

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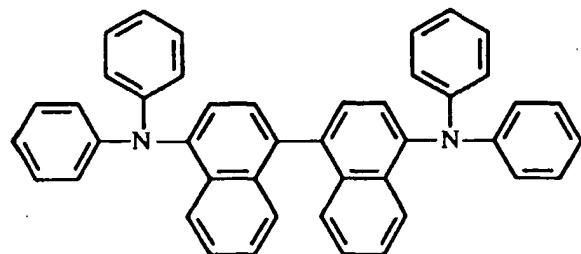
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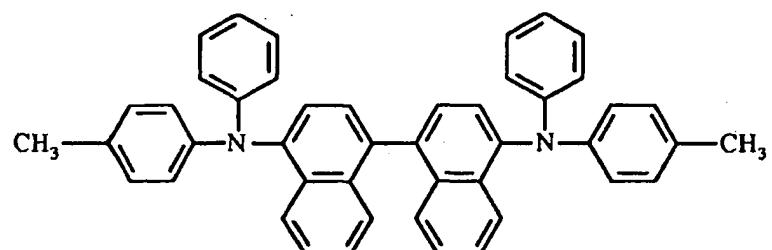
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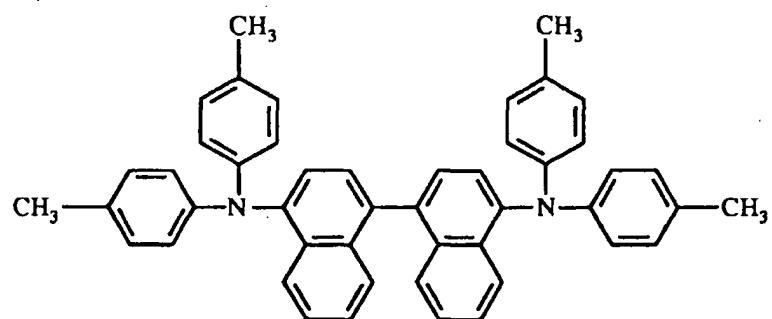
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(ATA-2)

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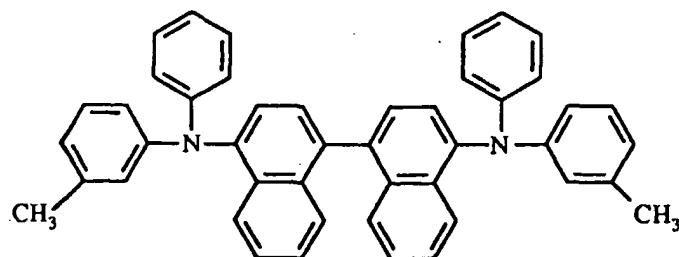


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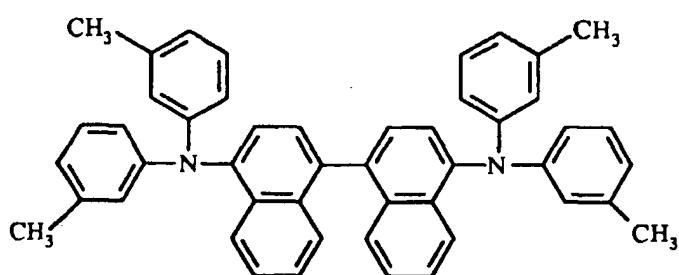
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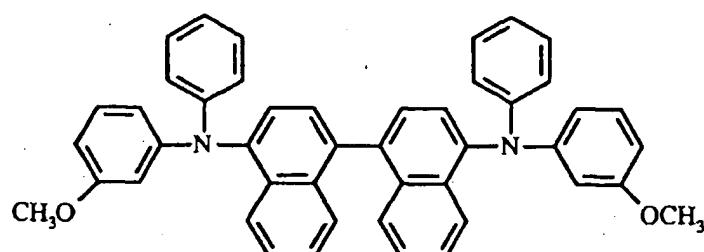
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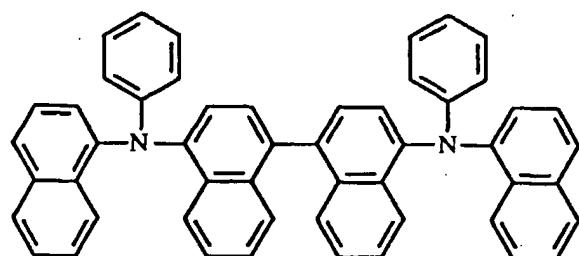
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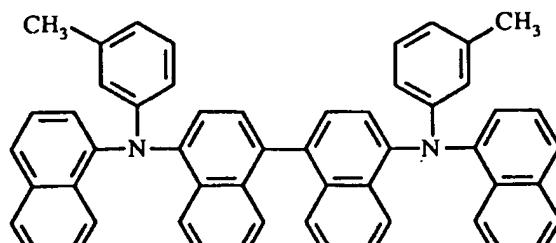
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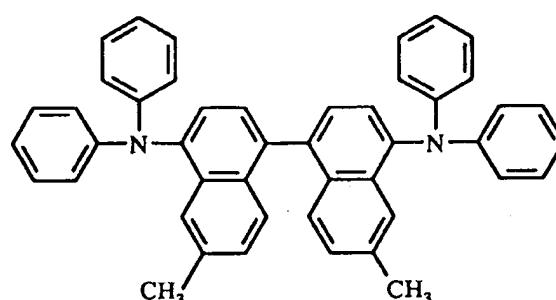
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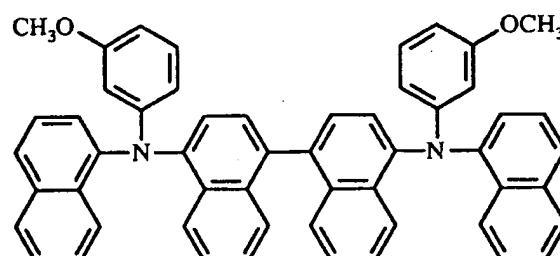
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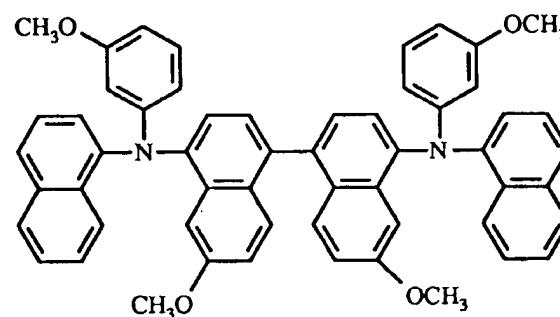
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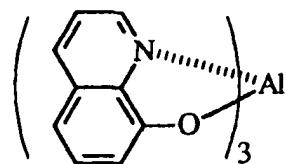
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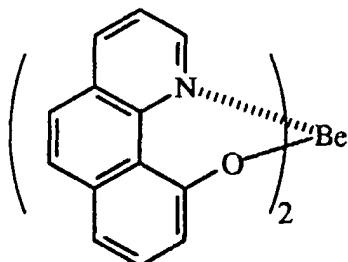
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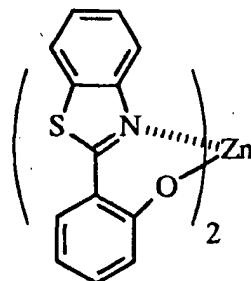
4. An organic electroluminescence device as claimed in claim 1, wherein the electron transporting layer (15) is composed of one of the following materials:



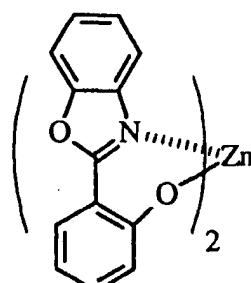
(Alq)



(BeBq)



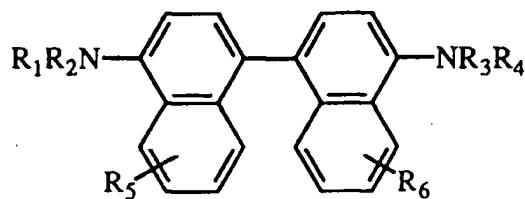
(ZnSPB)



(ZnOPB)

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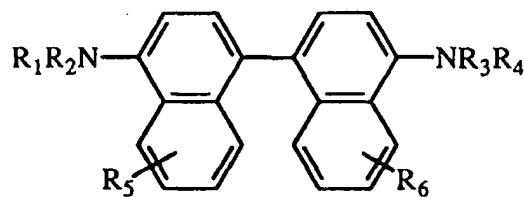
5. An organic electroluminescence device as claimed in claim 1, wherein the hole transporting layer (13) includes two layers of hole transporting materials and at least one layer of the hole transporting material is selected from the substance represent by the following formula 1



10 (Formula I)

15 where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.

20 6. An organic electroluminescence device as claimed in claim 1, wherein the hole transporting layer (13) includes a layer of mixed hole transporting materials, at least one of the hole transporting materials being selected from a substance represented by the following formula I



30 (Formula I)

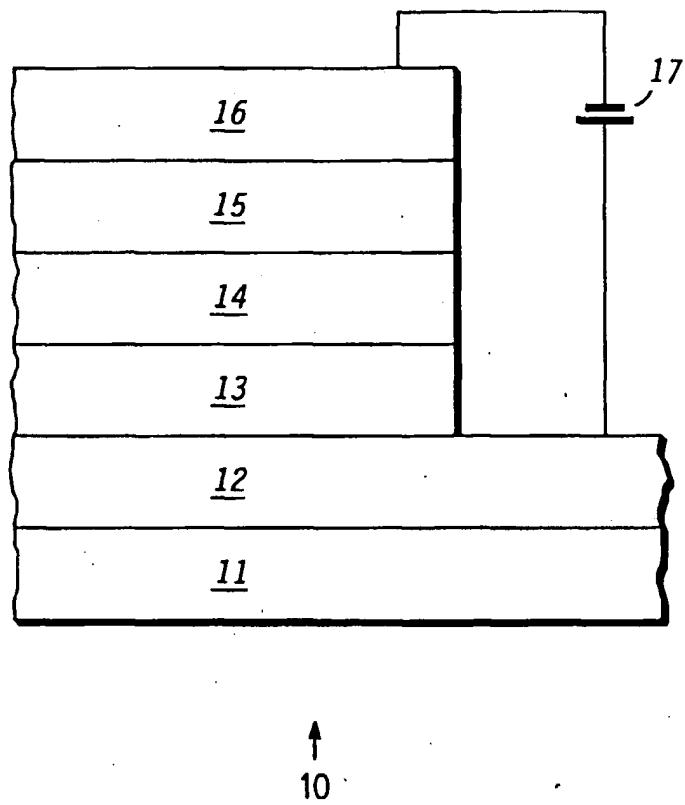
35 where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.

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- So, Franky
Tempe, Arizona 85284 (US)
- Lee, Hsing-Chung
Calabasas, California 91302 (US)

(30) Priority: 19.03.1996 US 616833

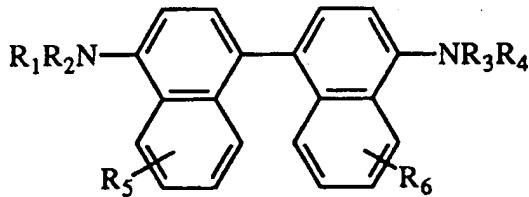
(74) Representative:
Gibson, Sarah Jane et al
Motorola
European Intellectual Property Operations
Midpoint
Alencon Link
Basingstoke, Hampshire RG21 7PL (GB)

(71) Applicant: MOTOROLA, INC.
Schaumburg, IL 60196 (US)

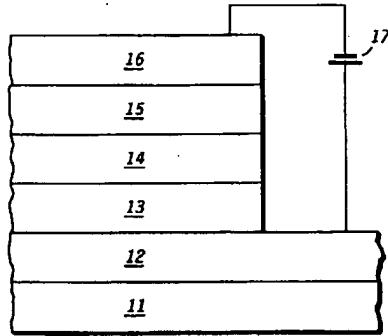
(72) Inventors:
• Shi, Song Q.
Phoenix, Arizona 85044 (US)

(54) Organic electroluminescent device with new hole transporting materials

(57) An organic EL device including a cathode (16), an electron transporting layer (15), an emitting layer (14), a hole transporting layer (13) and an anode (12) laminated in sequence. The hole transporting layer (13) includes a substance represented by:



(Formula I)



where R₁, R₂, R₃, R₄, R₅, R₆ each independently represent a hydrogen atom, an alkyl group of from 1 to 6 carbon atoms, a halogen group, a cyano group, a nitro group, or an aryl group of from 6 to 15 carbon atoms, a fused aromatic group, an alkoxy group, an alkylamine group, an aryloxy group, or an arylamine group.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 97 10 3641

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A, P	EP 0 731 625 A (EASTMAN KODAK) * the whole document *	1, 2, 4, 5	H05B33/14 H05B33/12 C07C211/58
E	EP 0 774 883 A (MOTOROLA) * the whole document *	1, 2, 4, 5	G03G5/06 H01L33/00
A, P	EP 0 713 148 A (MITA INDUSTRIAL) * the whole document *	1, 2, 4, 5	
TECHNICAL FIELDS SEARCHED (Int.Cl.6)			
H05B C07C G03G H01L			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	20 January 1998	Drouot, M-C	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			